80. *The Determination of "Active" Hydrogen.*

By Ernest A. Braude and E. S. Stern.

A convenient method for carrying out the determination of active hydrogen, using a simple nitrometer and diethyl ether as solvent, is described.

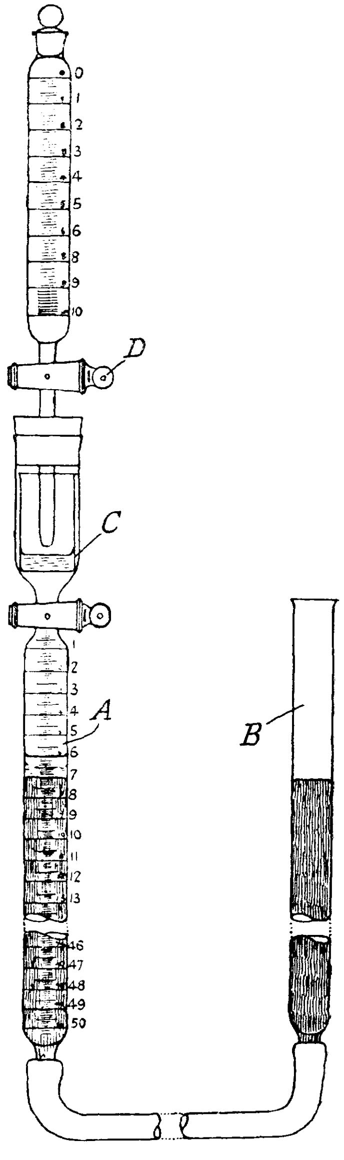
In connection with the analysis of reaction products in some kinetic investigations (Braude, Jones, and Stern, preceding paper) the need arose for an accurate and rapid method of determining "active" hydrogen, *e.g.*, the proportion of carbinol in carbinol–ether mixtures. The use of the reaction with methylmagnesium iodide in ethereal solution for analytical purposes was first suggested by Tschugaeff (*Ber.*, 1902, **35**, 3912), the volume of methane evolved being measured. The method was further developed by Hibbert and Sudborough (*J.*, 1904,

85, 933) and by Zerewitinoff (*Ber.*, 1907, **40**, 2023), who substituted di*iso*amyl ether for diethyl ether as the solvent on account of the high vapour pressure of the latter, and found it essential to work in an oxygen-free atmosphere. Other solvents, such as anisole and pyridine, have been tried, but di*iso*amyl ether has continued to be employed (cf. Hollyday and Cottle, *Ind. Eng. Chem. Anal.*, 1942, **14**, 774). The preparation of the di*iso*amyl ether reagent is laborious owing to the difficulty of rendering the solvent completely anhydrous and free from *iso*amyl alcohol, it is relatively expensive and it does not keep over long periods without special precautions. Moreover, the apparatus is cumbersome, and tedious to clean and dry. A method has now been developed using diethyl ether as solvent in which these disadvantages are overcome and which requires no special apparatus other than a simple nitrometer. It is only applicable, however, to relatively non-volatile compounds with functional groups reacting completely at room temperature.

TABLE I.

Values of $10^{-3}a$.

	Atm. press., mm. Hg.										
Temp.	750.	752.	754.	756.	758.	760.	762.	764.	766.	768.	770
14°	44·3	44·1	43·9	43·7	43·5	43·2	43·0	42·8	42·6	42·4	42·2
15	45·9	45·7	45·5	45·3	45·0	44·8	44·6	44·4	44·1	43·9	43·7
16	47·7	47·4	47·2	47·0	46·7	46·5	46·2	46·0	45·7	45·5	45·3
17	48·8	49·6	49·3	49·0	48·8	48·5	48·3	48·0	47·7	47·5	47·2
18	52·6	52·3	52·0	51·7	51·4	51·1	50·8	50·5	50·3	50·0	49·7
19	55·7	55·4	55·0	54·7	54·4	54·1	53·7	53·4	53·1	52·8	52·5
20	59·0	58·6	58·2	57·8	57·5	57·1	56·8	56·4	56·0	55·7	55·4
21	62·8	62·4	62·0	61·5	61·1	60·7	60·3	59·8	59·5	59·1	58·8



EXPERIMENTAL.

The reagent is prepared by reaction of methyl iodide (35 g., 1/4 mol.) with excess of magnesium (*ca.* 8 g.) in sodium-dry ether (200 ml.) and decanting the liquid into a 300-ml. brown-glass, stoppered bottle from which air has been displaced by oxygen-free nitrogen. After some hours the reagent is re-decanted and the volume made up to 250 ml. This reagent will keep for several months if excessive contact with air is avoided.

Determinations are carried out in an ordinary 50-ml. nitrometer filled with dry mercury and fitted with a rubber stopper carrying a small graduated dropping funnel (see fig.). About 0·5 ml. of dry ether is placed above the mercury in *A*. The sample (*ca.* 50—200 mg.) is accurately weighed into a wide specimen tube which is placed at *C*, 2 ml. of dry ether are added, and the stopper and funnel are replaced. The mercury level in *A* is adjusted to the zero mark and tap *D* is closed. The apparatus is tested for leaks by moving *B* up and down about equal distances and for about equal periods, after which the level in *A* should return to zero. 3 Ml. of reagent are then placed in the funnel, *B* is lowered, and about 2 ml. of reagent are allowed to enter drop by drop by manipulating tap *D*, until no further reaction takes place. The level in *B* is then adjusted slightly above that in *A*, the apparatus is set aside for 3—5 minutes, and *B* is then levelled and the volume read in *A*. If tap *D* is greased, a blank must be carried out, which should not exceed 2 ml. per ml. of reagent used. In normal circumstances, provided draughts be excluded and the room temperature be not too high, constant readings can be obtained over periods of at least 15 mins. No difficulties arising from the slow absorption of oxygen by the reagent have been experienced. The volume of the air present is small and is mainly driven over into the nitrometer by the methane evolved.

The reading in *A* — (vol. of reagent run in) — (blank reading, if any) = volume of methane evolved at a pressure equal to atmospheric pressure (p) — vapour pressure of diethyl ether (p'), at the temperature of the experiment. The theoretical volume of methane per atom of "active" hydrogen is given by

$$v_H = \frac{\text{Wt.}}{\text{Mol. Wt.}} \times 22{,}400 \times \frac{p}{p - p'} \times \frac{T}{273} = a \times \frac{\text{Wt.}}{\text{Mol. Wt.}}$$

Conversion factors a for a range of temperatures and pressures, calculated from vapour-pressure data given by Taylor and Smith (*J. Amer. Chem. Soc.*, 1922, **44**, 2450), are given in Table I. Determinations with six standard substances gave consistent results within ± 1—2% (Table II).

TABLE II.

Substance.	Wt. (mg.).	Temp.	p (mm.).	$v_{\text{obs.}}$ (ml.).	v_H (ml.).	$v_{\text{obs.}}/v_H$.
*cyclo*Hexanol	70·0	20°	765	39·1	39·3	0·99
	70·5	20	765	40·0	39·6	1·01
Benzyl alcohol	57·7	20	761	29·5	29·4	1·00
	63·2	20	761	33·0	33·3	0·99
Phenol	59·6	17	761	30·7	30·7	1·00
	56·1	17·5	761	28·9	29·6	0·98
Quinol	29·7	21	765	31·9	16·1	1·98
	30·4	21	765	32·6	16·5	1·97
Acetic acid	45·7	16	763	35·8	35·1	1·02
	46·9	16	763	36·7	36·0	1·02
Benzoic acid	54·7	20	761	31·5	31·1	1·02
	55·2	20	761	30·5	31·4	0·97

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W.7.

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